

THERMOELECTRIC MATERIALS WITH THE SKUTTERUDITE STRUCTURE: NEW RESULTS

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Skutterudite semiconductors possess attractive transport properties and have a good potential for achieving high ZT values. A large number of **isostructural** compounds, solid solutions and related phases are investigated. These **skutterudite** compositions offer many possibilities for substantially reducing the lattice thermal conductivity and for optimizing the electrical properties to a specific temperature range of thermoelectric applications. An overview of **recent** results is provided and current approaches to **experimentally** achieving high ZT in **skutterudite** materials are discussed.

Introduction

A systematic search for new thermoelectric materials was started at JPL several years ago. A family of compounds with the **skutterudite** crystal structure was identified as a good candidate for high **performance** conversion **efficiency** [1]. In **skutterudites**, the bonding is predominantly covalent [2], which accounts for the high carrier **mobilities** experimentally obtained on several compounds such as **CoAs₃** [3], **CoSb₃** [4, 5], **IrSb₃** [6], **RhSb₃** [5,7], **RhAs₃** [3] and **RhP₃** [8]. Also, the relatively large unit cell indicates that a low lattice thermal conductivity might be achieved. The **skutterudite** structure, illustrated in Figure 1, was originally attributed to a mineral from **Skutterud** (Norway) with a general formula (Fe, CO, Ni) **As₃** [9].

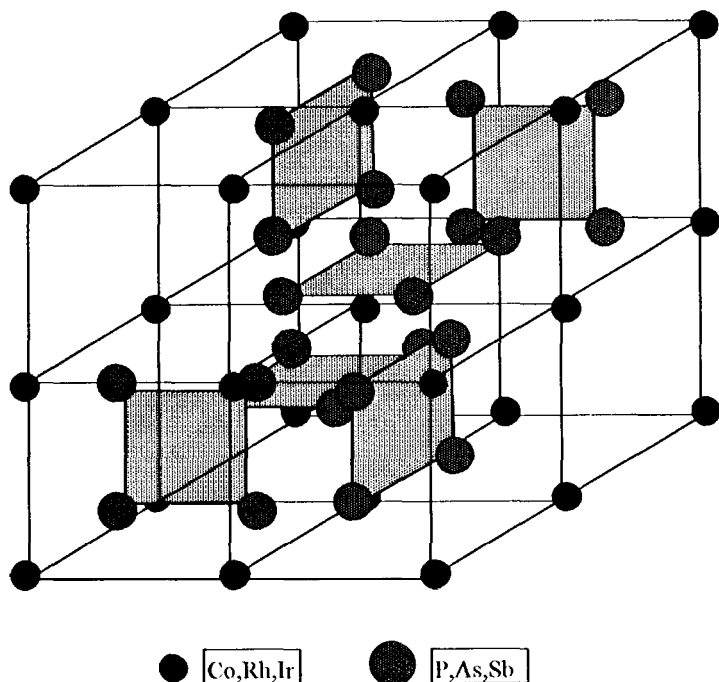


Figure 1: The skutterudite unit cell of formula TPn_3 (T = transition metal, Pn = pnictogen).

The unit cell of the **skutterudite** contains square radicals $[As_4]^{4-}$. This anion located in the center of the smaller cube is surrounded by 8 Co^{3+} cations. The unit cell was found to consist of 8 smaller cubes (octants) described above but two of them do not have the anions $[As_4]^{4-}$ in the center. This is necessary to keep the ratio $Co^{3+}:[As_4]^{4-} = 4:3$. Thus, a typical coordination

structure results with $Co_8[As_4]_6 = 2Co_4[As_4]_3$ composition and 32 atoms per cell with 8 AB_3 groups.

For the state of the art thermoelectric materials such as **PbTe** and **Bi₂Te₃** alloys, the number of **isostructural** compounds is limited and the possibilities to optimize their properties for maximum performance in different temperature ranges of operation are also very limited. This is not the case for **skutterudites** which show a variety of decomposition temperatures, band gaps and compositions which offers the possibility to optimize composition and doping level for a specific temperature range. **Skutterudite** compounds, solid solutions and related phases are briefly reviewed in the following sections.

Existence and composition of skutterudites

Binary compounds. Binary skutterudite compounds are formed with all nine possible combinations of the elements Co, Rh, Ir with P, As, Sb. In this structure each metal atom has six bonds to a pnictogen and each of three pnictogens has two bonds to another pnictogen. Thus, each bond has two electrons which is consistent with the fact that they are diamagnetic semiconductors [10].

Table 1. Lattice parameter a, decomposition temperature T_m , band gap E_g , Hall mobility μ_H and thermal conductivity λ of binary skutterudite compounds

Compound	a (Å)	T_m (°C)	E_g (eV)	reference
CoP ₃	7.7073	>1000	0.43*	11
CoAs ₃	8.2043	960	0.69*	3
CoSb ₃	9.0385	850	0.63*	5
RhP ₃	7.9951	> 200		8
RhAs ₃	8.4427	>1000	>0.85*	3
RhSb ₃	9.2322	900	0.80*	5
IrP ₃	8.0151	> 200		11
IrAs ₃	8.4673	> 200		12
IrSb ₃	9.2533	1141*	1.18*	6
NiP ₃	7.819	>850	metallic	13
PdP ₃ IP ₃	7.705	>650	metallic	13

* JPL findings

Known values for the lattice parameter, peritectic decomposition temperature and band gap of these nine binary compounds are reported in Table 1. Decomposition temperatures for CoP₃, RhP₃, RhAs₃, IrP₃ and IrAs₃ are only lower limit estimates. We have calculated the band gap values of

IrSb₃, RhSb₃, CoSb₃, RhAs₃, CoAs₃, and CoP₃ from high temperature Hall effect measurements. The p-type RhAs₃ sample was still not fully intrinsic at the highest temperature of measurement, thus the value of 0.85 should only be considered a lower limit. Less heavily doped samples must be obtained to accurately determine the band gap of RhAs₃. The value obtained for CoP₃ is only preliminary because the sample used for measurement contained CoP₂ inclusions. The only other binary skutterudites known are NiP₃ and PdP₃ which have one more electron valence per formula unit and consequently show metallic conduction [13]. For the arsenides and antimonides, the band gap increases in sequence from the Co- to the Ir-based compounds as well as from the antimonides to the arsenides.

Ternary compositions. Skutterudite related phases can be formed by substitution by neighboring atoms for the anion or the cation in binary skutterudite compounds, the condition being that the valence-electron count remains constant. This is similar to the diamond-like family of semiconductors. The substitution can occur on the anion site (CoAs₃ → CoGe_{1.5}Se_{1.5}) or on the cation site (CoSb₃ → Fe_{0.5}Ni_{0.5}Sb₃). Structurally related skutterudite phases can also be formed by partial substitution of the cation and the anion (RhSb₃ → RuSb₂Te).

Table 2: Skutterudite related phases

Compound	a (Å)	T _m (°C)	E _g (eV)	Reference
CoGe _{1.5} Se _{1.5}	8.017	1000		[14]
CoGe _{1.5} Se _{1.5} *	8.299	800		[14]
CoSn _{1.5} Te _{1.5} *	-	-		
RhGe _{1.5} Se _{1.5}	8.2746	>800		[15]
IrGe _{1.5} Se _{1.5}	8.297	>800		[15]
IrGe _{1.5} Se _{1.5} *	8.5591	>800		[15]
IrSn _{1.5} Se _{1.5}	8.7059	>800		[15]
IrSn _{1.5} Te _{1.5} *	-	-		
Fe _{0.5} Ni _{0.5} Sb ₃ *	9.0904	729 *	~0.16*	[16]
Fe _{0.5} Pd _{0.5} Sb ₃ *	9.2060*	-		
Fe _{0.5} Pt _{0.5} Sb ₃ *	9.1950*	-		
Ru _{0.5} Ni _{0.5} Sb ₃ *	9.1780*	-		
Ru _{0.5} Pd _{0.5} Sb ₃ *	9.2960*	647 *	-(0.6)*	[17]
Ru _{0.5} Pt _{0.5} Sb ₃ *		-		
Fe _{0.5} Ni _{0.5} As ₃	8.256	-		[18]
FeSb ₂ Se*			-	
FeSb ₂ Te*	9.112*	556*	-0.27*	
RuSb ₂ Se*	9.257*		-	
RuSb ₂ Te*	9.268*	810*	1.20*	
PtSn _{1.2} Sb _{1.8}	9.390	-		[19]

* JPL findings

Nine ternary skutterudite related phases have been reported in literature [14-19]. Based on X-ray diffraction analyses, eleven new compositions were discovered at JPL. A number of isostructural quaternary and more complex compositions have also been identified. Values for the lattice parameter a, decomposition temperature T_m and band gap E_g are reported in Table 2.

Solid solutions. The only solid solutions between binary skutterudite compounds reported in the literature show that CoP₃ and CoAs₃ form a complete range of solid solutions which obey the Vegard's rule and that the system CoAs_{3-x}Sb_x has a miscibility gap in the region of x = 0.4 to 2.8 [20]. Work at JPL on CoSb₃-IrSb₃ compositions also demonstrated that a partial range of solid solutions exists in this system [21]. Our more recent experimental results, summarized in Table 3, have shown that there is an extensive number of skutterudite compounds and related phases form solid solutions, at least in some limited range of composition.

Table 3. Existence of skutterudite solid solutions

Solid Solutions	Partial Range of Compositions	Full Range of Compositions
CoP ₃		CoAs ₃ *
CoAs ₃	CoSb ₃ *, IrAs ₃	
CoSb ₃	CoAs ₃ *, IrSb ₃ , Fe _{0.5} Ni _{0.5} Sb ₃ , FeSb ₂ Te	
RhSb ₃		IrSb ₃
IrAs ₃	CoAs ₃ , IrSb ₃	
IrSb ₃	CoSb ₃ , IrAs ₃	RhSb ₃ , RuSb ₂ Te
Fe _{0.5} Ni _{0.5} Sb ₃	CoSb ₃ , IrSb ₃ , Ru _{0.5} Pd _{0.5} Sb ₃	Ru _{0.5} Pd _{0.5} Sb ₃
Ru _{0.5} Pd _{0.5} Sb ₃	CoSb ₃ , IrSb ₃	Fe _{0.5} Ni _{0.5} Sb ₃
FeSb ₂ Te	CoSb ₃ , RuSb ₂ Te	
RuSb ₂ Te	FeSb ₂ Te	IrSb ₃

literature results

Filled skutterudites. A large number of these materials have already been synthesized (see for example [22-25]). The composition of these types of compounds can be represented by the formula LnT₄Pn₁₂ (Ln = rare earth, Th; T = Fe, Ru, Os; Pn = P, As, Sb). In these compounds, the empty octants of the skutterudite structure (see Figure 1) which are formed in the TPn₃ (~T₄Pn₁₂) framework are filled with a rare earth element. Because the T₄Pn₁₂ groups using Fe, Ru or Os are electron-deficient relative (by 4 e-) to the skutterudite electronic structure (using Co, Rh or Ir), the introduction of the rare earth atom compensates this deficiency by adding free electrons. However, the number of valence electrons given up by the rare earth atoms is generally insufficient: for example, La has a 3+ oxidation state, Ce can be 3+ or 4+. This means that most of these compounds behave as metals, or very heavily doped p-type semiconductors. However, it has been shown that some of them such as UFe₄P₁₂ and CeFe₄P₁₂ are semiconductors [22]. The addition of a new ion(s) in the voids could be an efficient phonon scattering center and could result in substantially lower lattice thermal conductivity values. The properties of such skutterudite compounds remain to be fully characterized.

Thermoelectric properties of skutterudites

Skutterudite compounds have exceptionally high hole mobilities, substantially higher than state-of-the-art semiconductors for a given carrier concentration. We have measured a Hall mobility value close to 8000 cm² V⁻¹ s⁻¹ on a p-type RhSb₃ single crystal

with a Hall carrier concentration of about $3.5 \times 10^{18} \text{ cm}^{-3}$. This is the **highest** p-type mobility ever measured at this doping level. All p-type skutterudites (binary and ternary compounds) investigated so far have high hole mobilities which make them very promising materials for thermoelectric applications.

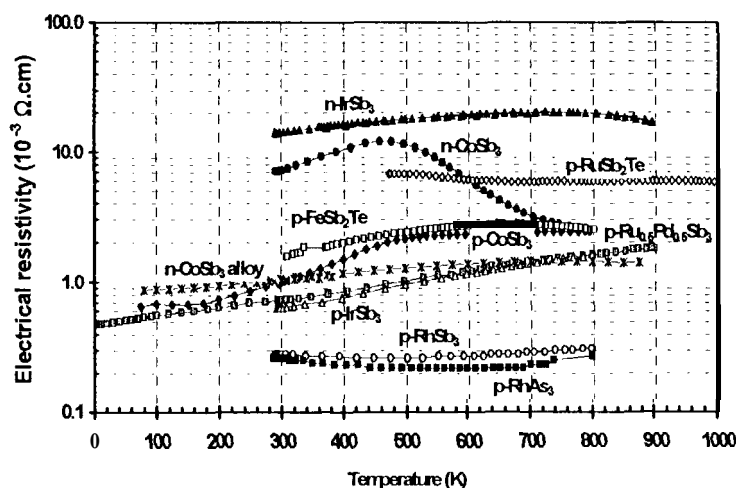


Fig. 2: Electrical resistivity as a function of temperature for several n-type and p-type skutterudite compounds.

N-type samples have been obtained for CoSb_3 and IrSb_3 by doping with elements such as Ni, Pd, Pt and Te [26, 27]. The Hall mobility of n-type samples was found to be much lower than for p-type materials, resulting in high electrical resistivity values. However, the large electron effective mass translated into high Seebeck coefficient, up to $500 \mu\text{V.K}^{-1}$ for n-type samples compared to only up to $200 \mu\text{V.K}^{-1}$ for p-type samples. As a consequence, optimum doping levels for n-type binary compounds are roughly one order of magnitude higher than for p-type skutterudites.

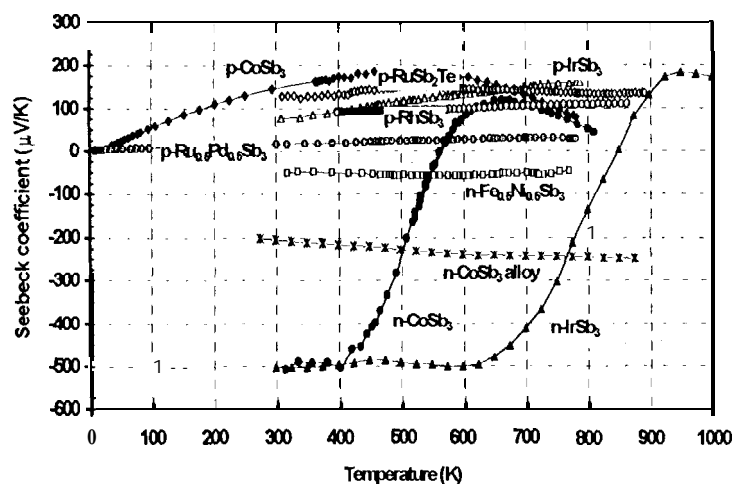


Fig. 3: Seebeck coefficient as a function of temperature for several n-type and p-type skutterudite compounds.

The experimental temperature variations of the electrical resistivity and the Seebeck coefficient of some binary skutterudites are shown in Figures 2 and 3, respectively. Minority carrier concentration effects (high mobility holes) are responsible for the change in Seebeck coefficient from positive

to negative at high temperatures for n-type CoSb_3 and IrSb_3 samples (Figure 3). Because of a smaller band gap, this compensation occurs at lower temperatures in CoSb_3 . The contribution from the minority carriers is much more limited in n-type CoSb_3 -based compositions prepared with high doping levels. This results in the Seebeck coefficient remaining n-type throughout the whole temperature range and a strong decrease in the electrical resistivity.

Almost no information about the thermal and electrical properties of ternary skutterudite related phases is available in the literature. Sonic results obtained at JPL on four ternary phases, FeSb_2Te , RuSb_2Te , $\text{Fe}_{0.5}\text{Ni}_{0.5}\text{Sb}_3$ and $\text{Ru}_{0.5}\text{Pd}_{0.5}\text{Sb}_3$ are reported in Figures 2 and 3. $\text{Fe}_{0.5}\text{Ni}_{0.5}\text{Sb}_3$ and FeSb_2Te are two ternary phases derived from CoSb_3 , and the calculated band gap values, 0.16 and 0.27 eV respectively, are much smaller than the 0.63 eV value for CoSb_3 . Similar results are obtained for $\text{Ru}_{0.5}\text{Pd}_{0.5}\text{Sb}_3$ (0.6 eV), which is derived from RhSb_3 (0.8 eV). The lower band gap values are consistent with the lower decomposition temperatures. This is not the case of RuSb_2Te however, which has a band gap of 1.20 eV.

The electrical properties of the ternary skutterudites also vary substantially from the results obtained on the binary compounds. It ranges from very heavily doped ($\text{Ru}_{0.5}\text{Pd}_{0.5}\text{Sb}_3$) to more lightly doped (RuSb_2Te), and from extrinsic p-type behavior (FeSb_2Te) to mixed conduction n-type behavior ($\text{Fe}_{0.5}\text{Ni}_{0.5}\text{Sb}_3$). These findings indicate that significant changes in band structure and doping behavior were brought by changes in the atomic and electronic structure, in particular, fluctuations in the valence of the transition metal atoms could be imposed by the need to conserve the skutterudite crystal structure. Understanding and controlling these changes is a key step in designing a skutterudite composition with superior thermoelectric properties.

Thermal conductivity

The thermal conductivity of p-type CoSb_3 , RhSb_3 and IrSb_3 samples was measured from 10 to 800 K [4, 26-27]. The results plotted in Figure 4 are compared to typical values obtained for state of the art thermoelectric alloys. Room temperature values of these three compounds range from 110 to 130 $\text{mW.cm}^{-1}\text{K}^{-1}$ depending on the carrier concentration level. These values are quite reasonable considering the relatively high decomposition temperature and bandgap of skutterudites (see Table 1). Additional measurements conducted on p-type CoAs_3 and RhAs_3 [3] indicated that the room temperature thermal conductivity values increase slightly from antimonides to arsenides, and also from Co-based compounds to Ir-based compounds. The Wiedemann-Franz law can be used to calculate the lattice thermal conductivity of p-type CoSb_3 , RhSb_3 and IrSb_3 samples. For a carrier concentration of a $1 \times 10^{19} \text{ cm}^{-3}$, calculations show that about 90% of the total thermal conductivity is due to the lattice contribution. Although we have not yet measured heavily doped n-type samples, the thermal conductivity of binary skutterudites appears to be too high to result in high ZT values. Experimental and theoretical results on p-type IrSb_3 showed that a maximum ZT value of 0.4 can be obtained at 900 K [28]. Reductions in the lattice thermal conductivity must be obtained to achieve values comparable to those of state of the art thermoelectric materials (10-40 $\text{mW.cm}^{-1}\text{K}^{-1}$).

Solid solutions possess a much lower lattice thermal conductivity due to atomic mass and volume fluctuations. However, a higher phonon scattering rate always has some

negative impact on the carrier mobility, but because the drop in thermal conductivity is usually larger than the degradation of the electrical properties, ZT values are overall substantially improved. This process has been used for all the state of the art thermoelectric materials, and is of interest for skutterudite compounds. Thermal conductivity measurements of several CoSb_3 - IrSb_3 alloyed samples showed that the thermal conductivity dropped to about $30\text{--}35\text{ mW}\cdot\text{cm}^{-1}\cdot\text{K}^{-1}$ at room temperature, a value 3 to 4 times smaller than for the individual compounds [21]. These results are also reported in Figure 4

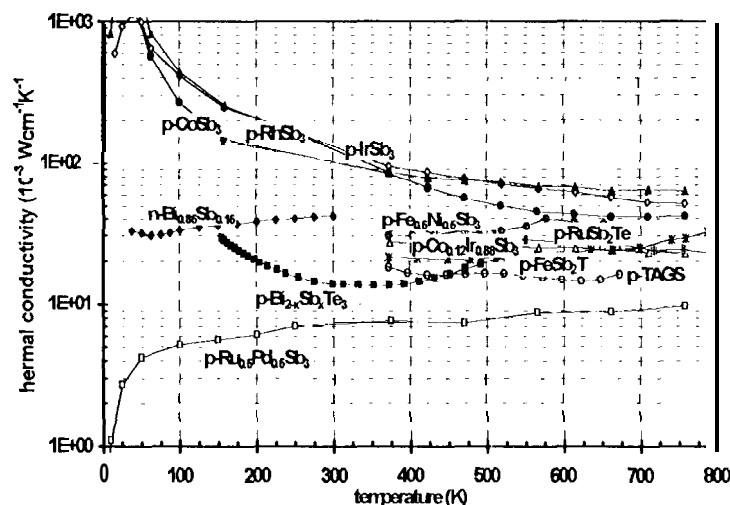


Fig. 4: Thermal conductivity as a function of temperature for several n-type and p-type skutterudite compounds, solid solutions and related phases.

As well as for solid solutions, the lattice thermal conductivity of ternary skutterudite phases was expected to be lower than for binary compounds. Our first results on six such ternary phases (five of them are new compositions) confirmed these predictions. JPL experimental data on four ternary phases, FeSb_2Te , RuSb_2Te , $\text{Fe}_{0.5}\text{Ni}_{0.5}\text{Sb}_3$ and $\text{Ru}_{0.5}\text{Pd}_{0.5}\text{Sb}_3$ are plotted in Figure 4. The thermal conductivity is greatly reduced in these materials, with room temperature values ranging from 7 to $30\text{ mW}\cdot\text{cm}^{-1}\cdot\text{K}^{-1}$. The low thermal conductivity values of these compounds, while very encouraging, are nevertheless a bit surprising considering that the atomic mass and volume differences introduced by the substituting anion/cation are fairly small. This indicates that additional mechanisms must be involved such as electron exchange scattering of phonons [29]. Of particular interest is the glassy behavior of $\text{Ru}_{0.5}\text{Pd}_{0.5}\text{Sb}_3$ where the thermal conductivity decreases with decreasing temperatures. At room temperature, the thermal conductivity value is $7\text{ mW}\cdot\text{cm}^{-1}\cdot\text{K}^{-1}$, about 15 times lower than for RhSb_3 (or IrSb_3). This is also lower than the values obtained for the state of the art thermoelectric materials. The lattice contribution was estimated at $2.5\text{--}3.0\text{ mW}\cdot\text{cm}^{-1}\cdot\text{K}^{-1}$, which is an extremely low value. However, this unoptimized material is still too heavily doped and the carrier concentration must be reduced to achieve larger Seebeck coefficient values.

Moreover, the possibility of forming solid solutions between these ternary compounds and the high mobility binary compounds (as described in Table 3) offers an excellent opportunity of finding a very low thermal conductivity material with good electrical properties. These results demonstrate the great potential of skutterudites for high ZT values as very high

nabilities, large Seebeck coefficients and very low lattice thermal conductivities can be obtained with materials of the same crystal structure.

Conclusion

A new family of promising thermoelectric materials with the skutterudite crystal structure has been presented. A number of binary compounds, solid solutions and ternary related phases have been briefly reviewed. Initial results obtained on some of their representatives demonstrated the great potential of skutterudites for high ZT values. Both p-type and n-type materials appear promising, though in a different range of carrier concentrations. If the good electrical properties of the binary skutterudite compounds can be somewhat preserved, there are several approaches for large reductions in thermal conductivity that could lead to ZT values substantially larger than 1.

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